Low-Hydrogen Silicon Oxynitride Optical Fibers Prepared by SPCVD

Eugene M. Dianov, Konstantin M. Golant, Rostislav R. Khrapko, A. S. Kurkov, and Alexander L. Tomashuk

Abstract—**The performance of the first samples of nitrogen-doped silica optical fibers, a novel type of optical fiber, is investigated. The fiber preforms containing up to ~3 at % of nitrogen in the core have been synthesized by reduced-pressure plasmachemical deposition (SPCVD) and drawn into fibers. By eliminating hydrogen-containing components from the gas mixture, low-hydrogen silicon oxynitride has been obtained. Optical loss in fibers in the range 1.3–1.6 μm, beyond OH- and NH-group absorption peaks, is several dB/km and, apparently, can be further reduced by optimizing the preparation processes.**

I. Introduction

UNTIL recently, the only use of silicon oxynitride as an optical material was in the fabrication of the core in integrated optics planar lightguides [1]. The merit of silicon oxynitride is the ability to vary refractive index over a wide range from 1.5–2.0 depending on the nitrogen and oxygen contents ratio in the glass net.

Silicon oxynitride planar lightguides are usually synthesized by plasma and nonplasma CVD-processes (e.g., see [2]), which ensure optical signal transmission in such several-centimeter long lightguides with a loss of several tenths of decibel. However, even in such short lightguides a tangible contribution to the loss in the wavelength region 1.3–1.6 μm is made by resonance absorption of O-H, N-H and/or Si-H bond overtones. This is due to the application of hydrogen-containing gases such as silane and/or ammonia in the CVD-processes. As a result, the synthesized silicon oxynitride contains a substantial proportion of hydrogen (up to 20 at %) which can be partially removed by way of heat treatment. However, even after a prolonged heat treatment at a relatively high temperature the hydrogen-associated added loss remains at the level of 1000 dB/km.

The application of hydrogen-containing reagents in CVD-processes is critical when it is necessary to deposit transparent silicon oxynitride films at relatively low temperatures of the gas and the substrate. A different situation arises with fiber preform synthesis which involves processes proceeding at temperatures much higher than 1000°C. On the one hand, one may employ high-purity chlorides and dry molecular oxygen as the raw materials, thereby drastically reducing the bonded hydrogen concentration in the glass. On the other hand, temperatures of about 2000°C, typical of the most widespread fiber-optic technologies such as MCVD, are too low to provide efficient dissociation of molecular nitrogen because of its large bond strength. In addition, silicon nitride Si_3N_4 dissociates at 1800°C, therefore the possibility of nitrogen incorporation into the glass net with the help of high-temperature CVD processes is highly conjectural.

A reduced-pressure glow-discharge PCVD-process utilizing silicon tetrachloride as the raw material makes it possible to overcome the above-stated problems and to synthesize hydrogen-free silicon oxynitride fiber preforms. A common feature of such processes is heterogeneous character of oxidation of silicon coming to the reaction zone in the form of $SiCl_4$ vapor. This means that the glass net formation is controlled by adsorption-desorption equilibrium in the substrate-gas system, not by condensation, thermophoretic transport of the SiO_2 soot and its fusion as with the MCVD-process.

An important advantage of a reduced-pressure glow-discharge PCVD-process over nonplasma processes is the presence of "hot" electrons capable of dissociating molecules by electron hit to supply a certain amount of chemically active radicals to the reaction zone. This feature opens up the possibility for the incorporation of atomic nitrogen into the glass net. In addition, a moderate temperature of the substrate surface during the deposition (about 1200°C) provides secure chemisorption of the atomic nitrogen by the growing silica layers.

To sum up, reduced-pressure plasmachemical deposition is the only possible technique for the fabrication of silicon oxynitride optical fiber using molecular nitrogen as a raw material. Recently, we have applied for the first time the SPCVD-process [3] to the fabrication of fiber preforms with a profile shaped by silicon oxynitride [4]. In this paper we discuss in more detail the technological process and optical loss spectra of the first fibers.

II. Plasmachemical Synthesis of Silicon Oxynitride Preforms

The distinctive feature of the SPCVD-process, a modification of the well-known PCVD-process, is that the layer-by-layer glass deposition is performed by varying periodically the length of the stationary plasma column sustained inside the substrate silica tube at the expense of the energy of traveling surface plasma waves. In our experiments the plasma column was excited by a microwave source with a power of 2–5 kW and a frequency of 2.45 GHz. The substrate tube temperature was measured by an optical pyrometer and maintained at 1240°C by an external heater. $SiCl_4+O_2+N_2$ gas mixture was fed into the tube toward the plasma column, the total pressure

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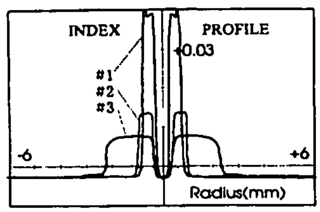

Fig. 1. Refractive index profiles in three silicon oxynitride preforms.

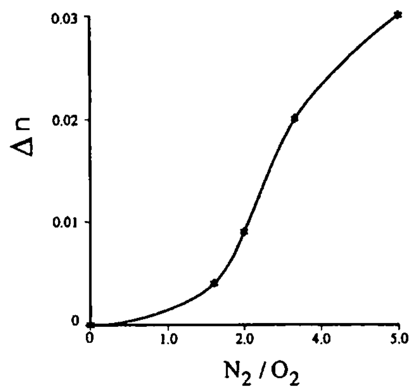

Fig. 2. Dependence of the refractive index difference in the synthesized glass with respect to undoped silica on the ratio of the N_2 and O_2 mass flow rates in the gas mixture. The $SiCl_4$ mass flow rate of 34 sccm was constant.

being several Torr. Each of the three reagents was fed through an individual gas-flow controller.

At first, undoped silica buffer layers were deposited during 2–3 h, oxygen being present in excess in the gas mixture. Then during 30 min or so silicon oxynitride layers were deposited. On completion of the deposition, the tube was collapsed into a preform with the help of an external torch. During the collapsing, the tube was blown through with dry oxygen under a slight excess pressure. After the collapsing the ratio of the diameters of the buffer and the core was 3:1.

Fig. 1 shows typical refractive index profiles in preforms. The central dip is larger than that in germanosilicate preforms and, obviously, is due to nitrogen burn-off during the collapsing. Clearly, the central dip can be removed through the use of fluorine etching during the collapsing process [5]. Outside the central dip the refractive index change reaches ~0.04, which corresponds to NA = 0.35. However, in order to have a high effective Δn, we had to deposit rather thick cores. For this reason, to produce a single-mode fiber, it was necessary to jacket a preform by silica tubes.

To estimate the nitrogen content in the sythesized glass, we used the relation between Δn and glass composition in silicon oxynitride thin films [6]. This relation suggests that $\Delta n = 0.04$ corresponds to glass composition $SiO_{1.94}N_{0.06}$.

The dependence of the refractive index difference on the ratio of N_2 and O_2 mass flow rates in the gas mixture is shown in Fig. 2. These data were obtained on a preform with a multistep profile. In preparing the preform, $SiCl_4$ and N_2 mass flow rates were kept constant, while the O_2 mass flow rate was changed stepwise several times, the combined N_2+O_2

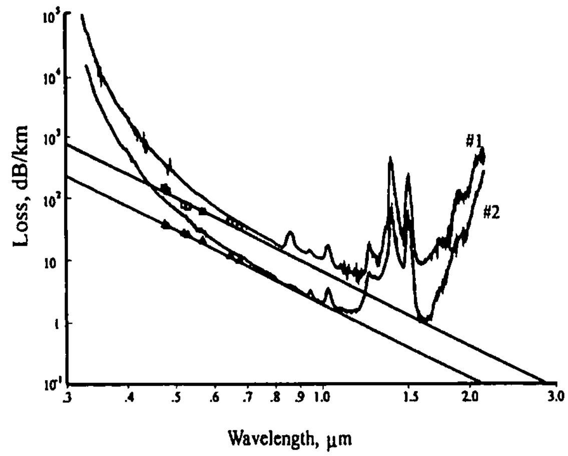

Fig. 3. Optical loss spectra in fibers #1 and #2. Squares (for fiber #1) and triangles (for fiber #2) indicate measured scattering loss. Straight lines approximate the spectral run of the scattering loss.

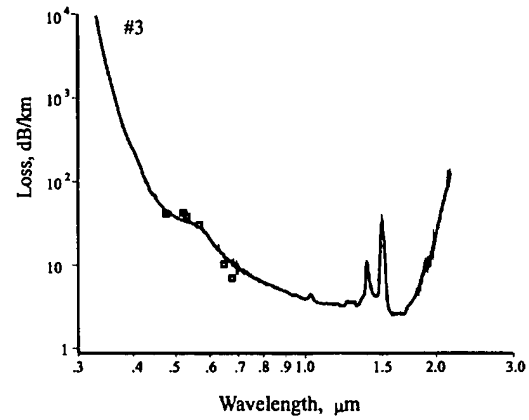

Fig. 4. Optical loss spectrum in fiber #3. Squares indicate measured scattering loss.

TABLE I
SILICON OXYNITRIDE FIBER PARAMETERS

Fiber	Type	Δn	Core Diameter, μm	Cut-Off Wavelength, nm
#1	single-mode	0.042	2	880
#2	single-mode	0.014	6	1480
#3	multimode	0.008	49	-

mass flow rate being always more than twice as large as the $SiCl_4$ mass flow rate. We notice that oxygen is substituted by nitrogen more efficiently under oxygen-deficient conditions. However, the mechanism of nitrogen incorporation into silica glass is not quite clear and calls for further investigation.

III. OPTICAL LOSS SPECTRA IN SILICON OXYNITRIDE FIBERS

The parameters of three fibers with different nitrogen concentrations are presented in the Table I, and their loss spectra plotted on a logarithm-logarithm scale, in Figs. 3 and 4.

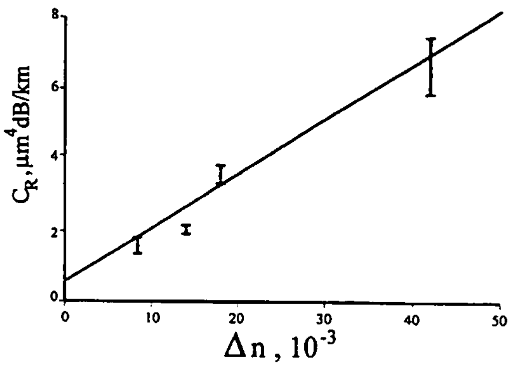

Fig. 5. Dependence of the Rayleigh scattering coefficients in silicon oxynitride fibers on the core/cladding refractive index difference.

The loss spectra were measured by the well-known cutback technique, the fiber pieces being up to ~1 km in length. At several spectral points, scattering loss was measured. The straight lines approximate the spectral run of the scattering loss α_{sc} ($\alpha_{sc} = C_R/\lambda^4$, where λ is the wavelength and C_R is the Rayleigh scattering coefficient).

First of all our attention is engaged by a rather low loss level in the near-IR region, the minimum loss being ~1 dB/km at $\lambda = 1.6\ \mu m$ (fiber #2). As regards the most important spectral region 1.3–1.55 μm, two loss mechanisms common to all the fibers are immediately apparent—Rayleigh scattering and OH- and NH-group absorption (in the case of NH-groups the first overtone peaks at $\lambda = 1.505\ \mu m$).

The presence of bonded hydrogen in the fibers is due to high humidity of the reagents and hydrogen diffusion from the jacketing tubes (in fibers #1, #2). The OH- and NH-group absorption is the strongest in fiber #1, because the distance of the cladding region formed by the jacketing tube from the core center is less than that in fiber #2. It is also apparent that the OH- and NH-group absorption must be the least in fiber #3 that was produced without the preform jacketing.

It is interesting that the OH- and NH-group absorption ratio in fiber #3 is indicative of preferential bonding of the hydrogen entering into the glass during deposition with nitrogen, not with oxygen. A reverse ratio of the absorption peaks in fibers #1, #2 is explained by the fact that in single-mode fibers a tangible share of light power propagates in the cladding. In addition, we believe that the hydrogen diffusing from the jacketing tube gathers mainly in the buffer cladding, where nitrogen is absent.

Rayleigh scattering in the fibers tested turned out to be several times greater than the typical values in germanium- and fluorine-doped silica fibers prepared by PCVD [7]. The Rayleigh scattering coefficients grow monotonically with increasing nitrogen content (Fig. 5).

Multimode fiber #3, unlike the other fibers, exhibited "grey" losses that might result from strong attenuation of higher-order and leaky modes (note a rather small Δn and a broad central dip).

Another interesting feature of fiber #3 is an absorption band with a maximum at $\lambda = 560$ nm. The color centers responsible for this band were found to luminesce. For this reason, the scattering loss was overestimated. The appearance of this absorption band may be associated with a much lower hydrogen content in fiber #3 than that in fibers #1 and #2.

IV. Discussion

The results testify that silicon oxynitride synthesized by a hydrogen-free reduced-pressure PCVD-process may be considered as a promising alternative material for fiber optics. Even the first tentative fibers have exhibited optical loss of several dB/km in the near-IR region.

A further loss reduction can be achieved above all by reducing hydrogen content in the glass. Estimations show that for a single-mode fiber with $\Delta n = 0.008$ the limit set by Rayleigh scattering is ~ 0.56 dB/km at $\lambda = 1.30\ \mu m$.

Further investigations are expected to provide the answer to the question as to whether such a strong Rayleigh scattering is inherent in silicon oxynitride fibers prepared by PCVD or it may be decreased by optimizing the preparation processes and the fiber profile. In this connection, of interest is the investigation of the mechanism of nitrogen incorporation into silica and the microstructure of the resultant glass.

V. Conclusion

The first silicon oxynitride optical fibers have been prepared by hydrogen-free SPCVD-process, the minimum loss in the fibers being several dB/km in the near-IR region. The two chief loss mechanisms have been revealed: strong Rayleigh scattering and OH- and NH-group absorption. The results give grounds to continue the investigation of the preparation regimes and performance of silicon oxynitride optical fibers as a possible alternative to the traditional types of optical fibers.[1]

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[1] While the paper was under consideration for publication, we fabricated a silicon oxynitride fiber with a loss of 0.3 dB/km at 1.55 μm. This was achieved by drying the reagents.

References

[1] C. H. Henry, G. E. Blonder, and R. F. Kazarinov, "Glass waveguides on silicon for hybrid packaging," *J. Lightwave Technol.*, vol. 7, pp. 1530–1539, 1989.

[2] F. Bruno, M. del Guidice, R. Recca, and F. Testa, "Plasma-enhanced chemical vapor deposition of low-loss SiON optical waveguides at 1.55 μm wavelength," *Appl. Opt.*, vol. 30, pp. 4560–4564, 1991.

[3] D. Pavy, M. Moisan, S. Saada, P. Chollet, P. Leprince, and J. Marrec, "Fabrication of optical fiber preforms by a new surface plasma CVD process," in *Proc. 12th European Conf. Optical Communication*, Barcelona, 1986, pp. 19–22.

[4] V. A. Bogatyrjev, E. M. Dianov, K. M. Golant, R. R. Khrapko, and A. S. Kurkov, "Silica fiber with silicon oxynitride core fabricated by plasmachemical technology," in *Proc. OFC '95*, San Diego, CA, 1995, paper ThH7.

[5] A. J. Ritger, "Bandwidth improvement in MCVD multimode fibers by fluorine etching to reduce the central dip," in *Proc. IOOC-ECOC '85*, Venezia, 1985, vol. 1, pp. 913–916.

[6] *VLSI Electronics Microstructure Science, Plasma Processing for VLSI*, N. G. Einspruch and D. M. Brown, Eds. Orlando, FL: Academic, vol. 8, 1984.
[7] P. Geittner, H.-J. Hagemann, and D. Leers, "Intrinsic scattering and absorption losses of Ge- and F-doped fibers prepared by PCVD," *Electron. Lett.*, vol. 25, pp. 436–437, Mar. 1989.

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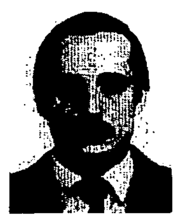

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